Limits on heterogeneous processing in the Antarctic spring vortex from a comparison of measured and modeled chlorine

D. T. Shindell[1] and R. L. de Zafra[2]

Physics Department, State University of New York, Stony Brook

Abstract. Forty-day photochemical model runs are compared with ground-based stratospheric ClO observations taken during the austral spring of 1993. Our purpose is to explore the range of required heterogeneous processing within which we can reproduce the duration and degree of chlorine activation within the Antarctic spring vortex. Heterogeneous processing on nitric acid trihydrate (NAT) polar stratospheric clouds (PSCs) or supercooled ternary solution (STS) -type particles is shown to be necessary to maintain chlorine in active forms during ozone hole formation in September, even for small HNO_3 amounts, or chlorine deactivates sooner than observed. The lower limits for the surface areas required are quite small, however. Thus the record ozone losses observed during September of 1993 may be attributed to catalytic loss due to chlorine maintained in active forms by heterogeneous processing despite the sparse particle loading of the Antarctic lower stratosphere at that time. The ozone loss rates predicted by the model during the formation of the springtime Antarctic ozone hole indeed agree quite well with observations. The one-dimensional model is also able to reproduce both the observed timing and rate for subsequent deactivation of chlorine. Renitrification from PSC evaporation is not required for this deactivation, as HCl reformation is very rapid at low ozone values.

Introduction

The Stony Brook millimeter-wave spectrometer was used to measure chlorine monoxide emission spectra from September 4 to October 9 over McMurdo Station, Antarctica, during the formation of the 1993 austral spring ozone hole [*de Zafra et al.*, 1995]. The duration during which chlorine remains in active forms, along with the amount of active chlorine present, determines the amount of ozone destruction which takes place. Our observations of the amount of active chlorine and the timing of its deactivation in the polar lower stratosphere are compared here with the behavior of a one-dimensional photochemical model over the same 40-day period. The model results are also checked against coincident balloon observations of ozone depletion [*Johnson et al.*, 1995]. The use of a one-dimensional model is justified by the isolation of the polar

vortex (as shown by National Meteorological Center (NMC) potential vorticity maps) during this period of stability well before vortex breakup. We use our measurements from well inside the polar vortex as representative conditions within the vortex, and compare them with the one-dimensional model foremost to examine the sensitivity of the model results as a function of various purely chemical parameters, including surface areas for heterogeneous reactions and reaction quantum yields.

Chlorine activation and its subsequent deactivation have been modeled previously [e.g., *Liu et al.*, 1992; *Crutzen et al.*, 1992; *Müller et al.*, 1994; *Douglass et al.*, 1995]. Measurements of ClO throughout the entire period being modeled were not available for comparison, however (though modeled HCl or ozone loss was compared with measurements). In addition, to the best of our knowledge, previous studies have not explored the issue of minimum surface areas required for heterogeneous processing to maintain adequate rates of chlorine activation, which we consider in the following sections.

Chlorine Monoxide Observations

ClO measurements were taken daily, weather permitting, at McMurdo Station, Antarctica (77° S, 166° E) from September 4 through October 9, 1993, as described in *de Zafra et al.* [1995]. NMC potential vorticity maps
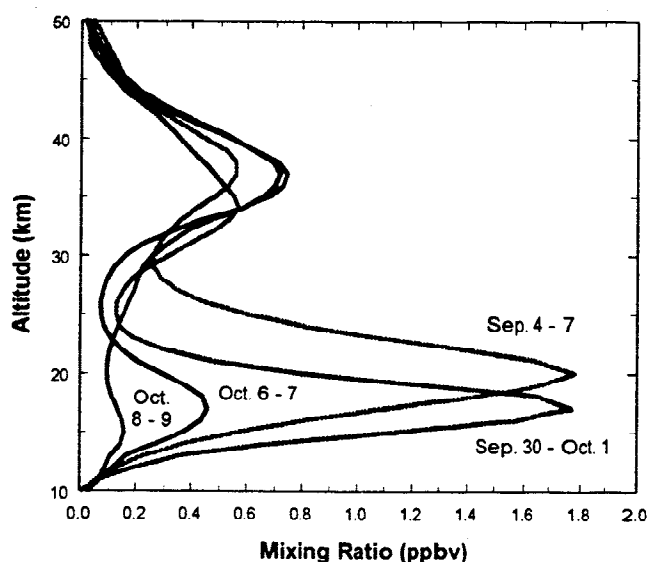
Figure 1. A sample of midday chlorine monoxide observations from McMurdo Station, Antarctica, averaged over the given days in 1993. The selected profiles show the persistence of the enhanced lower stratospheric layer throughout September, followed by its rapid decrease in early October.

show that McMurdo was well inside the lower stratospheric polar vortex throughout this period, except for a brief period around September 25 when the inner edge of the vortex reached McMurdo. An enhanced lower stratospheric layer of chlorine monoxide was observed, peaking at a mixing ratio of about 1.8 parts per billion by volume (ppbv) for midday-minus-predawn values at 20 km on September 4, when our first measurements were made. This layer remained at approximately the same maximum mixing ratio, within our total measurement uncertainty of ~12% [de Zafra et al., 1995], until October 1. The altitude of the mixing ratio peak however, descended several kilometers during this period. Severe weather conditions interrupted our data acquisition on October 2. By October 6 and 7, when we were able to resume measurements, the mixing ratio of ClO at 18 km altitude had dropped to ~0.44 ppbv midday-minus-predawn, further diminishing to only ~0.12 ppbv midday-minus-predawn by October 8 and 9. A sample of ClO vertical profiles retrieved from these data is shown in Figure 1. Since these data were all taken within the lower stratospheric vortex, they are a direct observation of the duration of chlorine activation, as well as its rapid deactivation at the beginning of October.

The measurements only sampled air parcels moving over a single location. However, as the vortex was rotating over us, we effectively sampled an entire latitude band (assuming roughly circular motion). At the latitude of McMurdo, the circumpolar transit time for vortex air at 18 km altitude is ~5-6 days (derived from NMC winds), so the observations throughout September sampled each longitude ~4-5 times. The consistency of the measurements therefore indicates that the chlorine activation inside the polar vortex

was fairly homogeneous at the latitude of McMurdo. The measurements of reduced ClO in October over McMurdo are therefore taken to be indicative of chemical deactivation rather than a dynamical process such as transport of unprocessed air.

Model Parameters

The behavior of chlorine species during September and October has been simulated with the one-dimensional photochemical model described by Shindell and de Zafra [1996]. The model has since been updated with the O_3 photolysis quantum yields of Ball and Hancock [1995]. The initializations given there have been used to set conditions for September 5, 1993. For the issues to be discussed here, the most important of these initializations are given in Table 1, for 18 km altitude, somewhat below the mixing ratio peak for this date (but at which altitude the mixing ratio of ClO remained roughly constant during September). Temperature (188 K at 18 km) and pressure have been taken from coincident University of Wyoming ozonesondes (B. Johnson, personal communication, 1993). The model has then been run for 40-day simulations. During these 40 days, temperatures were varied in accordance with NMC data for McMurdo, shown in Figure 2. A comparison of NMC data and local ozonesonde temperatures showed quite good agreement, with no systematic bias. In essence, the temperature at 18 km remained constant from September 6 to 17, increased gradually by ~8 degrees over the period September 18 to 28, then increased rapidly by another 6 degrees over the period September 29 to October 2, remaining roughly constant thereafter. Simple geometrical

Table 1. Initial Values at 18-km Altitude

Species	Mixing Ratio	Species	Mixing Ratio
ClO	1.5 ppbv	HNO_3	1.3 ppbv
Cl_2O_2	0.9 ppbv	H_2O	2.5 ppmv
HCl	0.04 ppbv	CH_4	0.8 ppmv
$ClONO_2$	0.02 ppbv	O_3	1.3 ppmv
HOCl	0.02 ppbv		
Cl_y	3.4 ppbv		

ClO: from our midday-minus-predawn observations; Cl_2O_2: in equilibrium with ClO (total Cl in ClO + $2\times Cl_2O_2$ is therefore 3.3 ppbv); HCl: small, as the total amount of inorganic chlorine present in the other chlorine species is already at the upper limit for Cl_y of Woodbridge et al., [1995] and von Clarmann et al. [1995]; $ClONO_2$ and HOCl: small, as these have been depleted by heterogeneous reactions on PSCs which were seen during August [Johnson et al., 1995]; HNO_3: near the lowest values from CLAES version 7 September 1992 measurements near McMurdo Station (J. Mergenthaler, personal communication, 1994); CH_4 and H_2O: from version 17 HALOE October 1993 measurements (J. Russell, personal communication, 1994); O_3: from coincident ozonesonde data (B. Johnson, personal communication, 1993).
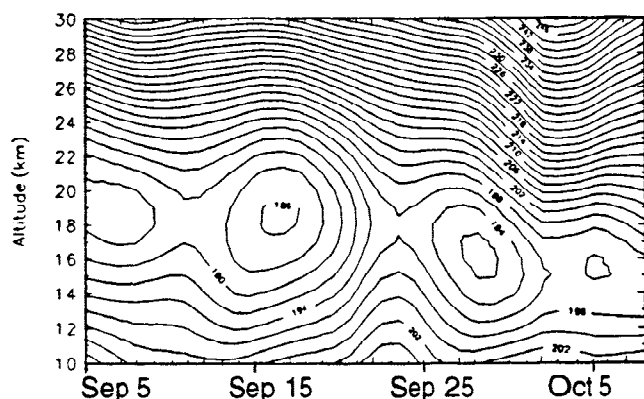
Figure 2. Temperature versus altitude from gridded NMC data for the McMurdo area. This figure has been reproduced from *de Zafra et al.* [1995].

downward motion has also been included. Descent rates of 50-80 m per day have been used, approximately matching the descent rate of the ClO vertical profiles that we observed, and in good agreement with model predictions for the southern vortex at this time of year [*Manney et al., 1994; Rosenfield et al., 1994*]. The descent in our model persists until October 1, the time of the rapid increase in temperature.

As noted by *Shindell and de Zafra* [1996], the downward transport in the lower stratosphere brings increased mixing ratios of ozone to a given altitude. This balances out the increased chemical destruction at a fixed altitude due to the lengthening of the day. It also counteracts the increase in the rate limiting three body dimer formation reaction in the ClO dimer catalytic cycle which results from the descent of the ClO peak concentration to regions of higher background pressure. These factors reconcile our observed descent of the ClO peak (leading to increasingly efficient catalysis of ozone) plus the increasing duration of solar exposure, with the observation of a roughly constant ozone loss rate [*Johnson et al.*, 1995].

Results and Discussion

No Heterogeneous Processing

Polar stratospheric clouds (PSCs) were relatively rare in the McMurdo area during September of 1993 [*Johnson et al.*, 1995], and we explore first the extent to which active chlorine can be maintained in the extreme case where all heterogeneous processing has ceased. Figure 3 displays several chlorine species and ozone at 18 km altitude for September and early October when the model has been run without heterogeneous chemistry. The chlorine species shown here are the dominant contributions to the total amount of inorganic chlorine, excluding the ClO dimer which has been omitted for clarity (an example of the dimer's rapid cycling is given later). The diurnal variation of ClO is due to the nighttime formation of the dimer

during the early part of the run. This gradually shifts to cycling between ClO and ClONO$_2$ toward the end of the run as temperatures increase and the ClO dimer becomes thermally less stable. The increased ClO abundance remaining at night around October 3 results from the increasing thermal instability of the dimer at this time, while ClONO$_2$ cycling is not yet very large as NO$_X$ is still small due to the long lifetime of HNO$_3$.

During this run, there was a steady conversion of chlorine from reactive ClO into the reservoir species HCl due to the reactions ClO + OH → HCl + O$_2$ and Cl + CH$_4$ → HCl + CH$_3$. Chlorine nitrate also formed through the reaction ClO + NO$_2$ + M → ClONO$_2$ + M, where the NO$_2$ sources are HNO$_3$ photolysis and reaction with OH. For this homogeneous chemistry run, an initial HNO$_3$ mixing ratio of 3.5 ppbv was used instead of the denitrified value of 1.3 ppbv given in Table 1 since there was no PSC formation. The net result is that the midday-minus-predawn mixing ratio of ClO has decreased to slightly more than one third of its initial value by October 1, in stark disagreement with our measurements, which show that ClO remained roughly constant, within our uncertainty,
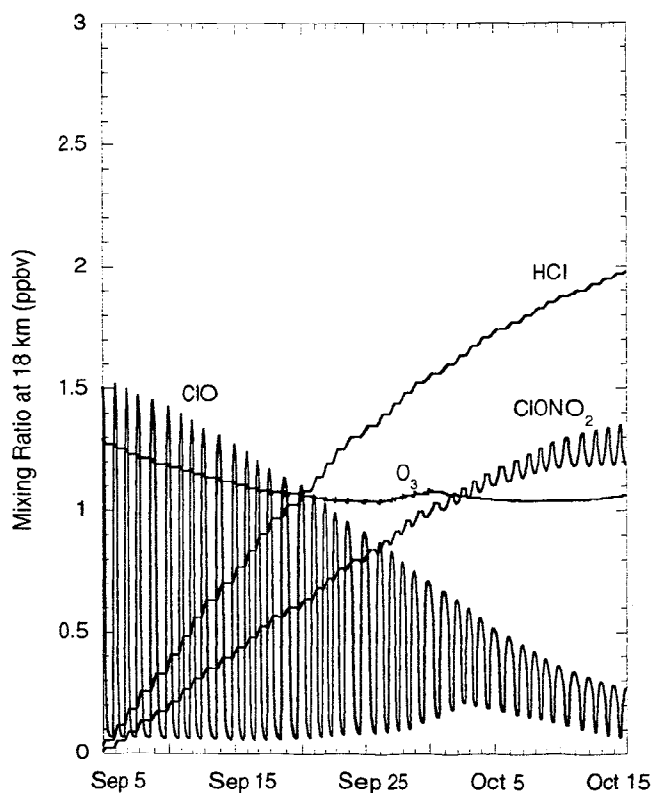

Figure 3. Modeled behavior of the most abundant chlorine species (with the exception of the ClO dimer, which has been left off for clarity) and ozone during the period of Antarctic ozone hole formation. The model has been initialized on September 5 with our ClO measurements. Heterogeneous chemistry has not been included in this run, while a geometrical descent rate of 50 m/d has been included.
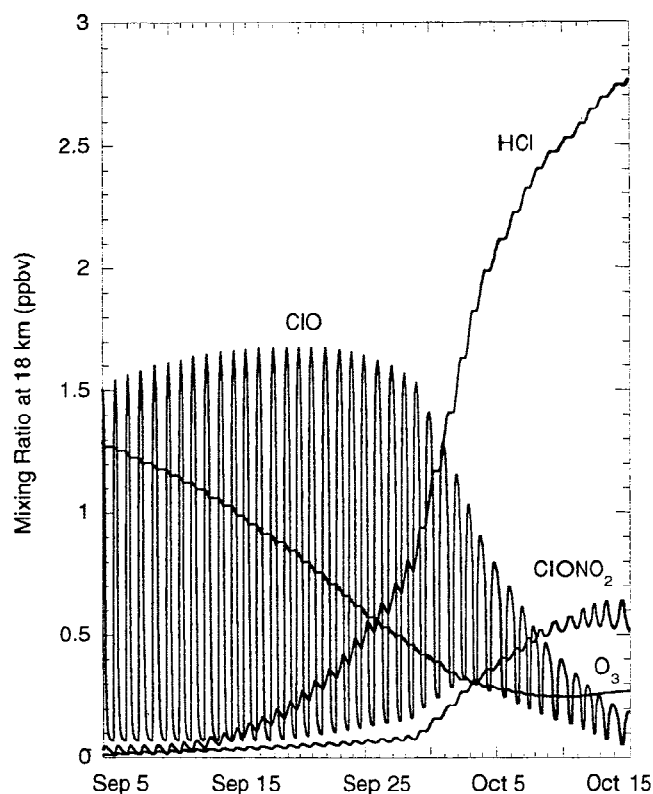
Figure 4. Modeled behavior of the most abundant chlorine species (with the exception of the ClO dimer, which has been left off for clarity) and ozone during the formation of the Antarctic ozone hole. The model setup is identical to that used in Figure 3, except including the presence of 1.0 $\mu m^2/cm^3$ NAT PSCs until September 29.

throughout September at 18 km altitude. The behavior of HCl in this run is also in strong disagreement with that seen in column measurements taken in 1993 at McMurdo by the New Zealand National Institute of Water and Atmospheric Research (NIWA) (K. Kreher and G. Keys, private communication, 1995), which show very low HCl through September, followed by a very rapid rise beginning about October 1. (See also 1987 and 1989 HCl column measurements of *Liu et al.* [1992].) Since the amount of HNO_3 primarily influences $ClONO_2$ through gas phase chemistry, the disagreement with ClO and HCl observations is similar even when a denitrified 1.3 ppbv HNO_3 is used. The ozone loss rate seen in this run is also in disagreement with observations, being only about one fifth that seen in ozonesonde data. In this run, the kink in the ozone line results from the (simplified) abrupt cessation of descent in the model on October 1.

In summary, without continuing heterogeneous processing throughout September, too much chlorine is transferred to HCl and $ClONO_2$ to maintain the measured large amounts of ClO and small amounts of HCl, or the rate of ozone loss observed, even in a denitrified lower stratosphere.

Heterogeneous Processing on NAT

Heterogeneous chemistry on PSCs which converts chlorine from reservoir to reactive species has been previously studied in long-run model studies [e.g., *Crutzen et al.*, 1992; *Müller et al.*, 1994]. As already noted in other studies, only a brief period of time in the presence of PSCs is sufficient for rapid processing to activate chlorine (see below), so that encounters elsewhere within the vortex could have been able to maintain the high ClO levels that we observed over McMurdo Station, and still be consistent with the paucity of PSC events seen there by balloon and lidar [*Johnson et al.*, 1995]. We present here the results of our model when nitric acid trihydrate (NAT) PSCs are included during September, with the intent of establishing a lower limit on the time- and space-averaged surface area needed to maintain chlorine activation at observed levels during the period of active ozone hole formation. Reaction probabilities on NAT were taken from the 1994 Jet Propulsion Laboratory recommendations [*DeMore et al.*, 1994].

The occurrence of PSCs over Antarctica is most likely during the winter polar darkness during June–August. A 10-year zonal average of Stratospheric Aerosol Measurement 2 data shows the probability for sighting a PSC (given as the number of clouds divided by the total number of observations) over Antarctica at 18-20 km altitude decreases from a maximum value of 0.6 in mid-August to 0.3 by mid-September [*Poole and Pitts*, 1994]. We note that UARS measurements within the Antarctic vortex, on which we have based the initializations used in our model whenever available (see caption accompanying Table 1 and *Shindell and de Zafra* [1996]), are indicative of a large amount of NO_x removal by heterogeneous processing on PSCs prior to September.

As PSC constituent species (H_2O and HNO_3) are depleted, formation temperatures drop, reducing the likelihood of PSC formation. On the other hand, ozone depletion may itself increase the likelihood of PSCs being present in September. The destruction of ozone removes the primary absorber of thermal radiation in the stratosphere. This creates a positive feedback loop where ozone loss leads to colder temperatures, which may extend the duration of the period when heterogeneous chemistry is effective in maintaining chlorine activation, as pointed out by *Solomon* [1990].

Figure 4 shows the evolution of the same chlorine species and ozone as in the previous figure for a model run including the presence of a constant 1.0 $\mu m^2/cm^3$ surface area of NAT PSCs per unit volume until the sharp temperature rise which was observed on September 29. At that point, the temperature increased rapidly past the NAT PSC evaporation temperature. In this run, the modeled midday-minus-predawn chlorine monoxide remained roughly constant until the end of September, after which it decreased fairly rapidly, in general agreement with our observations. During September, there is some buildup of HCl (Cl_y is conserved, since the HCl increase is
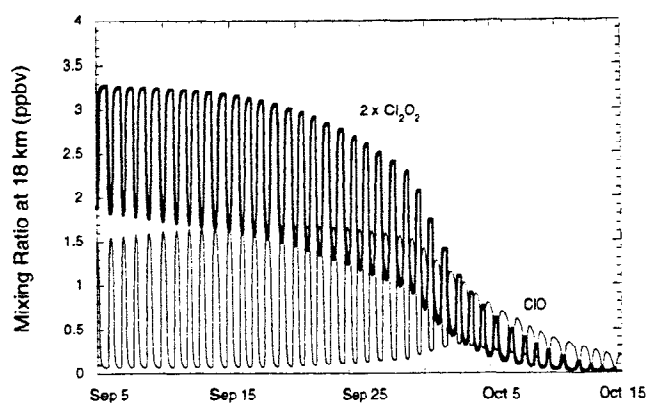
Figure 5. Modeled behavior of ClO and Cl_2O_2 for the same heterogeneous chemistry run as in Figure 4.

compensated for by a decrease in the amount of chlorine in Cl_2O_2 with increasing temperature, see Figure 5). The modeled HCl now follows the general pattern of the NIWA observations at McMurdo in September-October, 1993, and also those from 1987 and 1989 [*Liu et al.*, 1992]. Figure 5 shows the ClO dimer along with ClO as an example of the diurnal cycling of the dimer during this heterogeneous chemistry run.

The modeled ozone loss in the heterogeneous chemistry run is also quite different from that in the homogeneous run. The heterogeneous run, which preserves chlorine in active forms throughout September, accurately reproduces the observed ozone behavior in airflow over McMurdo. This showed a roughly linear decrease until the first week of October, by which time it was nearly totally destroyed in the 18-20 km layer [*Johnson et al.*, 1995]. The depletion rate of the ozone layer from 10 to 24 km resulting from model runs is an approximately constant 3.3-4.3 Dobson units (DU) per day in PSC run, depending on the descent rate chosen (from 80 to 50 m/d). This is in good agreement with the roughly linear 4.1 DU/d loss in this layer measured by balloon sondes [*Johnson et al.*, 1995] in both the amount of depletion and the time at which depletion ceased.

In the model, PSC processing was stopped on September 30, consistent with the rapidly rising temperature seen after that date. In this run, HNO_3 from NAT PSC evaporation was not reinserted into the model. Measurements show that relatively little nitric acid returns after temperatures have warmed enough for PSCs to evaporate [*Roche et al.*, 1994; *Van Allen et al.*, 1995; *de Zafra et al.*, this issue], and particle formation models predict that many of the PSCs forming early in the winter accrete to such large sizes that they are removed from the lower stratosphere by gravitational settling by springtime [e.g., *Drdla and Turco*, 1991]. These results are consistent with the overall picture from the photochemical model, in that renitrification of the stratosphere is not required for the deactivation of chlorine. The specific influences of renitrification and low ozone chemistry on the reservoir reformation process are discussed in more detail below.

The model has also been run with $3.0 \, \mu m^2/cm^3$ NAT PSC surface area present for 24 hours every sixth day to simulate an encounter with a PSC once per circumpolar circuit made by an air parcel (as when only one region is cold enough for PSCs, as can occur due to orographic forcing). The results are shown in Figure 6. The cyclic processing which takes place is sufficient to keep chlorine predominantly in active forms throughout September. Note that the time averaged surface area for this intermittent processing is only one half that required for constant loading, as the surface area is 3 times larger, but present for only one sixth the amount of time. While this type of oscillation in the maximum ClO mixing ratio was not seen in our observations, the variations in the case presented here are at the uncertainty level of our data, and would, furthermore, be somewhat washed out in the 2-3 day averaging of midday data which we typically use to increase the signal-to-noise ratio in our data.

Despite record O_3 losses over Antarctica during September 1993, PSC observations at McMurdo were relatively sparse [*Johnson et al.*, 1995]. We have shown here that the lower limit for spatially and time-averaged PSC surface areas for heterogeneous processing required to
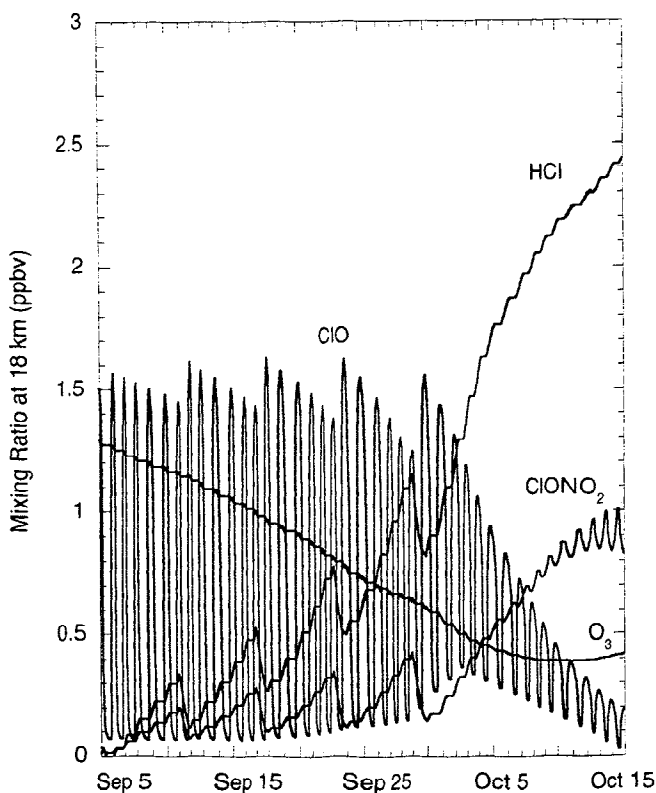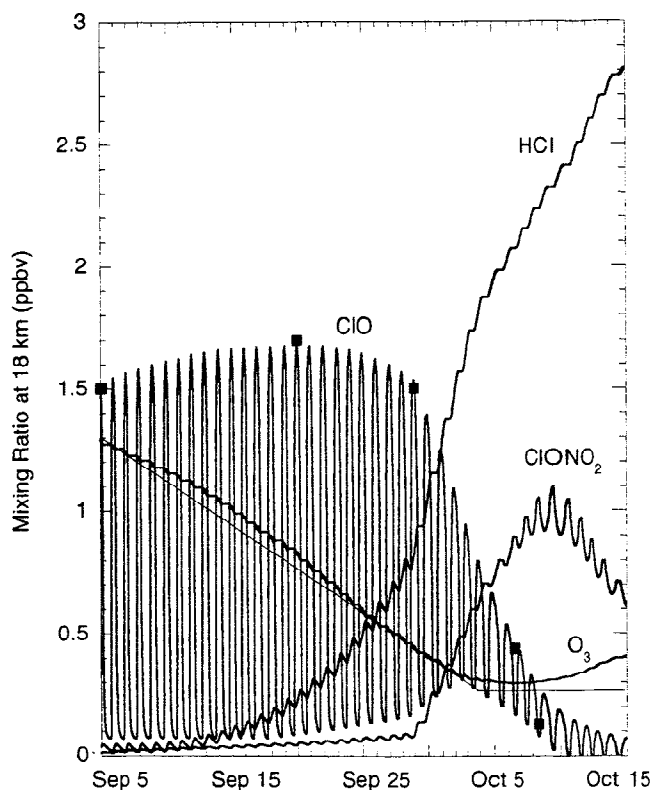

Figure 6. Modeled behavior of the most abundant chlorine species (with the exception of the ClO dimer, which has been left off for clarity) and ozone during the formation of the Antarctic ozone hole for a model run similar to that shown in Figure 4, except with a $3.0 \, \mu m^2/cm^3$ PSC encountered every 6 days until September 29.

Figure 7. Modeled behavior of the most abundant chlorine species (with the exception of the ClO dimer, which has been left off for clarity) and ozone during the formation of the Antarctic ozone hole for a model run identical to that shown in Figure 4, except including renitrification from the evaporation of PSCs after September 29. The squares are our measured ClO values at 18 km on the indicated days, while the solid line represents a linear fit to the ozone balloon data [*Johnson et al.*, 1995] which were taken approximately every 2 days.

maintain chlorine in active forms is actually quite small, so that the paucity of PSCs seen in 1993 was likely still enough to account for the large levels of active chlorine observed, and hence led to severe ozone loss. The greater amounts of PSCs seen in previous years were likely overkill as far as heterogeneous activation of chlorine was concerned. PSCs may also have been present elsewhere, giving the required spatially averaged surface area for processing.

Reservoir Reformation

The model has also been run including renitrification of the lower stratosphere from PSC evaporation. This was accomplished by increasing the value of HNO_3 at 18 km altitude from 1.3 to 3.5 ppbv when temperatures rose past the PSC evaporation threshold, the large value corresponding to the values seen by CLAES in mid-September 1992 at the end of their southern-looking observations. The results are shown in Figure 7. The NAT

PSC surface area was again set to a constant $1.0 \ \mu m^2/cm^3$.

While more chlorine nitrate forms in early October during this run, due to the increased HNO_3 (and hence NO_x), chlorine partitioning by mid-October is approximately the same. In general, there is competition in the formation of reservoir chlorine between HCl and $ClONO_2$. In the runs which include heterogeneous chemistry, and hence realistically simulate the destruction of ozone, HCl is the dominant reservoir, but only appears in substantial amounts around the end of September. In the run containing only homogeneous chemistry (Figure 3), $ClONO_2$ reached a much larger abundance. The difference is due to the heterogeneous reactions of $ClONO_2$ with HCl and H_2O, as well as the effect of differing amounts of ozone persisting until October, which alters the chemistry of the NO_x family as outlined by *Prather and Jaffe* [1990]. When the concentration of ozone is extremely low, as in October in the heterogeneous runs, the reaction $NO + O_3 \rightarrow NO_2 + O_2$ is suppressed, so that the partitioning of NO_x shifts to favor NO over NO_2. The excess NO shifts the balance of Cl, ClO, and $ClONO_2$ to favor Cl by increasing $ClO + NO \rightarrow NO_2 + Cl$, while $Cl + O_3 \rightarrow ClO + O_2$ is also suppressed by lack of ozone and $ClO + NO_2 + M \rightarrow ClONO_2 + M$ is suppressed by lack of NO_2. This creates a situation where the formation of HCl via the reaction of Cl with CH_4 dominates over the chlorine nitrate forming reaction of ClO and NO_2. The lifetime of HCl is longer than that of $ClONO_2$ as well, leading to the partitioning of inorganic chlorine almost entirely into HCl, with only minimal values of $ClONO_2$ at the end of the polar spring if ozone is severely depleted. The greater ozone depletion in the southern vortex than the northern thus leads to interhemispheric differences in reservoir reformation, with HCl reformation proceeding more rapidly in the Antarctic than in the Arctic, as seen in UARS data [*Douglass et al.*, 1995]. The similarity of the two heterogeneous chemistry runs with constant PSC surface area (Figures 4 and 7) shows that with severely depleted ozone, the model's sensitivity is primarily to the low ozone chemistry, and much less to whether or not renitrification takes place.

The modeled midday-minus-predawn ClO during the October deactivation actually agrees somewhat better with our measurements when renitrification is included. Given the limitations inherent in modeling a vortex-wide phenomenon with a one-dimensional model, along with the uncertainties in NO_y initializations, as well as in our own measurements, we can only conclude that deactivation either with or without renitrification agrees qualitatively with our observations. We note however, that in the run with renitrification, the mixing ratio of ClO at 18 km altitude has dropped to about 0.5 ppbv by October 6-7, and to about 0.3 ppbv by October 8-9, so that reasonable quantitative agreement with the rapid depletion seen in our measurements (see Figure 1) can certainly be obtained.

The reservoir reformation process is also quite sensitive to the chemical reaction rate parameters used in the model. One of the most important uncertainties is that of the
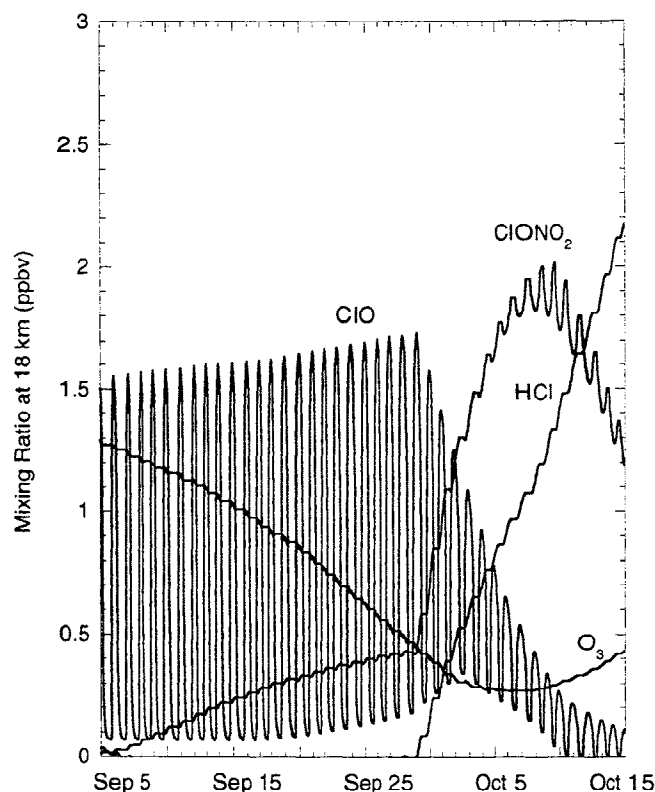
Figure 8. Modeled behavior of the most abundant chlorine species (with the exception of the ClO dimer, which has been left off for clarity) and ozone for a model run similar to that shown in Figure 7, except that the branching ratio of ClO + OH → HCl +O$_2$ has been reduced from 10% to zero.

quantum yield of the reaction pathway ClO + OH → HCl + O$_2$, with laboratory measurements only setting an upper limit at ~15% [*DeMore et al.*, 1994]. The model run shown in Figure 7 used a quantum yield of 10% for HCl from this reaction. The results in the extreme case when the yield of HCl from this reaction is set to zero are shown in Figure 8. The overall behavior of ClO is similar to that of Figure 7, though with a slightly increased value at the end of September when reservoir reformation has already begun, and a slightly decreased ClO value in mid-September when heterogeneous chemistry is rapid. The latter change results from the ClO + OH → HCl + O$_2$ reaction allowing for more efficient heterogeneous processing, as also found by *Lary et al.* [1995]. The behavior of the reservoirs shows quite high sensitivity to this quantum yield, however. While heterogeneous chemistry is taking place, HCl is now destroyed more rapidly than it is created, so that its concentration becomes extremely small. The heterogeneous reaction of ClONO$_2$ with HCl then becomes insignificant, so that ClONO$_2$ reacts heterogeneously only with H$_2$O, and therefore builds up slowly. Note that the individual influences of the two ClONO$_2$ heterogeneous reactions can be seen clearly from a comparison of three runs: the homogeneous chemistry run

(Figure 3), including neither reaction, this run with the HCl yield from ClO + OH set to zero (Figure 8), which effectively includes only the heterogeneous reaction of chlorine nitrate with water, and the previous heterogeneous run (Figure 7), which included both ClONO$_2$ heterogeneous reactions. After PSC evaporation and renitrification, the transfer to reservoirs is again rapid in this zero quantum yield run, though much more strongly toward ClONO$_2$ than in the previous run. Owing to the lack of ClO sensitivity to this quantum yield, we cannot differentiate between the runs on the basis of our measurements, however.

Other reaction uncertainties may be significant as well. Recent measurements indicate that the yield of HCl as a product from the reaction of ClO with HO$_2$ is also possible, with an upper limit of 5% on this branching ratio (M. Finkbeiner, personal communication, 1995). Adding this channel for HCl formation would have an influence similar to that of the larger ClO + OH → HCl + O$_2$ yield on the relative rates of formation of reservoir species, favoring HCl at the expense of ClONO$_2$ during chlorine deactivation.

The influence of the timing of the removal of PSCs on reservoir reformation can be seen in Figure 9, which shows the results of a model run similar to that shown in Figure
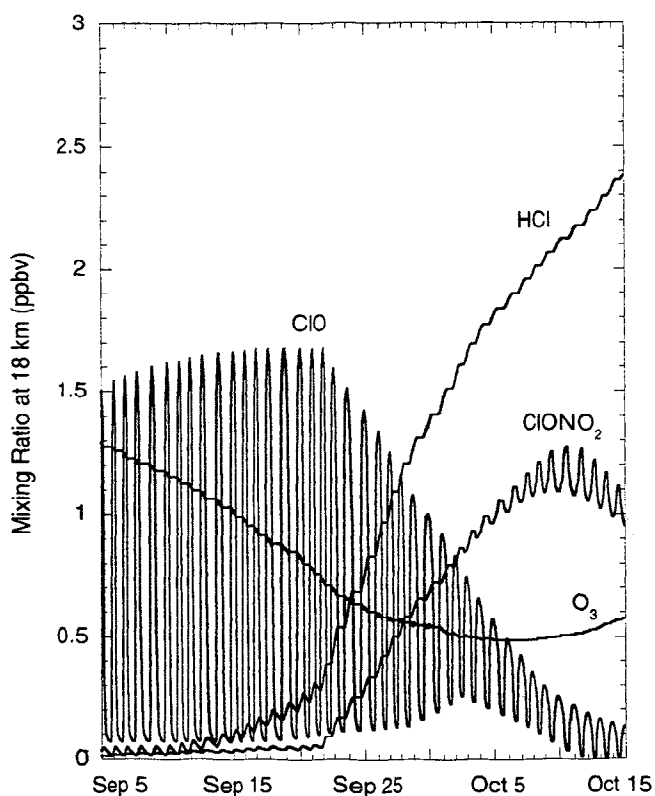

Figure 9. Modeled behavior of the most abundant chlorine species (with the exception of the ClO dimer, which has been left off for clarity) and ozone for a model run similar to that shown in Figure 7, except that PSC processing has been stopped on September 22.

1448 SHINDELL AND DEZAFRA: LIMITS ON HETEROGENEOUS PROCESSING

7 (including renitrification), except with PSCs removed on September 22 instead of September 29. Chlorine deactivates much more slowly after the cessation of heterogeneous chemistry, as less hydroxyl is present at the earlier date since the solar exposure is less, leading to slower $ClO + OH \rightarrow HCl + O_2$ and slower $HNO_3 + OH \rightarrow H_2O + NO_3$ (which leads to $ClONO_2$ formation). More chlorine nitrate and less HCl now forms during October since there has been less severe ozone destruction and hence the ozone depletion effect on chemistry described previously is less significant here. We conclude that the modeled reservoir reformation process is quite sensitive to both the amount of ozone remaining and to the chemical reaction rate parameters used in the model, and somewhat less sensitive to the amount of renitrification and to the timing of the end of heterogeneous processing. Provided that heterogeneous chemistry continues long enough however, the chlorine deactivation rate is relatively insensitive to these variables, and all the cases presented here show general agreement with our deactivation measurements.

Heterogeneous Processing on STS

The discussion of heterogeneous chemistry thus far has been restricted to reactions taking place on the surfaces of NAT PSCs. Heterogeneous processing can also take place rapidly on the surfaces of supercooled ternary solutions (STS), made up of water, nitric acid, and sulfuric acid. The STS particle sizes of *Carslaw et al.* [1994], and temperature dependent reaction probabilities on STS surfaces (D. Hanson, personal communication, 1995) have also been used in the model. The surface areas of *Carslaw et al.* [1994] are in fact much larger than is necessary to partition chlorine completely into active forms. They calculate a surface area ~20 $\mu m^2/cm^3$ at 188 K, in the presence of 5 ppbv HNO_3 assumed for the Arctic (though there is significantly less nitric acid present in the Antarctic springtime lower stratosphere). At this temperature, we find that a surface area of ~1 $\mu m^2/cm^3$ is sufficient for nearly full chlorine activation in the photochemical model.

In a 40-day run with STS, chlorine is maintained in active forms until approximately September 23, similar to the results seen in Figure 9, and in disagreement with our observations. After this date, the increasing stratospheric temperature causes both the reaction probability on an STS surface and the STS surface area itself to decrease dramatically, accounting for the earlier cessation of heterogeneous processing than in the NAT PSC runs.

Summary

A comparison between 40-day model results and ground-based observations of ClO at McMurdo Station for the austral spring of 1993 indicates that a one-dimensional model containing realistic rates of downward transport can reproduce the duration of chlorine activation deep within the lower stratospheric polar vortex only when heterogeneous processing continues throughout September. Without heterogeneous chemistry, modeled chlorine deactivates earlier than is observed, even in a denitrified lower stratosphere. Lower limits have been set on both the surface areas of NAT PSCs and STS droplets which are necessary to maintain chlorine in active forms in accordance with observations. Including heterogeneous chemistry, the model is able to reproduce both the timing and the rate of chlorine deactivation in accordance with the observations, with or without the inclusion of renitrification following PSC evaporation, as HCl reformation is very rapid when ozone has been severely depleted.. We have shown that the reformation of reservoir species is quite sensitive to the degree of ozone depletion and to the values of reaction rate parameters used, and somewhat sensitive to the timing of the cessation of heterogeneous processing and the degree of renitrification. The ozone loss rates predicted by the heterogeneous chemistry model were shown to agree quite well with observations during formation of the springtime Antarctic ozone hole, even with small particle surface areas similar to those observed.

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R. L. de Zafra, Physics Department and Institute for Terrestrial and Planetary Atmospheres, State University of New York at Stony Brook, Stony Brook, NY 11794.

D. T. Shindell, NASA GISS/Columbia University, 2880 Broadway, New York, NY 10025. (email: dshindel@giss.nasa.gov)